

Low-energy electron collisions with biomolecules

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2012 J. Phys.: Conf. Ser. 388 012017

(<http://iopscience.iop.org/1742-6596/388/1/012017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 131.215.71.79

The article was downloaded on 21/03/2013 at 15:55

Please note that [terms and conditions apply](#).

Low-energy electron collisions with biomolecules

Carl Winstead and Vincent McKoy

Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena,
California 91125, USA

E-mail: carl@schwinger.caltech.edu, mckoy@caltech.edu

Abstract. We report recent progress in applying the Schwinger multichannel computational method to the interactions of slow electrons with biomolecules. Calculations on constituents of DNA, including nucleobases, phosphate esters, and models of the backbone sugar, have provided insight into the nature of the low-energy shape resonances, and thereby into possible sites and mechanisms for electron attachment that may lead to strand-breaking. At the same time, more approximate calculations on larger assemblies such as nucleosides and deoxyadenosine monophosphate indicate how the resonance properties of the subunits will or will not persist in DNA itself. We are pursuing a similar strategy for another major class of biomolecules, the proteins, by beginning with fixed-nuclei studies of the constituent amino acids; here we present preliminary results for the simplest amino acid, glycine. We also describe efforts directed at an improved understanding electron collisions with alcohols, which, in addition to basic scientific interest, may prove useful in the modeling of ignition and combustion within biofuel-powered engines.

1. Introduction

The discovery that slow electrons induce strand breaks in DNA through resonant processes [1, 2, 3, 4] has inspired an outpouring of studies, both experimental and computational, seeking to understand key mechanistic questions: Where do electrons initially attach? What is the nature of the temporary anions formed? How do the electron and nuclear dynamics couple to cause strand breaks or other damage? By now much relevant information has been gained, and, while we do not yet have definitive answers to such questions, we do have plausible models that further work can aim to support or refute. For example, Simons and coworkers have explored an indirect strand-breaking process in which the initial attachment is to a nucleobase π^* resonance [5, 6, 7, 8, 9], consistent with the work of Martin *et al* [10], who discern a correlation between the strand-break spectrum and the distribution of π^* resonances. On the other hand, direct attachment to the backbone has also been proposed [11], and gas-phase experiments have demonstrated that low-energy dissociative attachment takes place in models of both the sugar and the phosphate moieties (e.g., [12, 13, 14]).

Electron-induced damage to biomolecules other than DNA is also attracting increasing study. As major structural and functional constituents of living tissue, proteins are a natural subject of interest; moreover, as polymers assembled from a small library of amino acids, they are amenable to the same approach as has been applied to DNA, beginning with computations and gas-phase experiments on the isolated subunits and working towards larger assemblies. Water, the simplest and most abundant biomolecule, also continues to be of interest. In a slightly different context, alcohols produced by fermentation of biomass are attractive alternatives to

fossil fuels used in transportation. Although methanol and, especially, ethanol are now most widely used, higher alcohols have combustion properties closer to those of gasoline and thus show great potential. Modeling of spark ignition and combustion in alcohol-fueled engines requires a database of reaction rates and collision cross sections, including electron collision data.

This paper briefly reviews some recent computational work on biomolecules using the Schwinger multichannel (SMC) method [15, 16] as implemented for parallel computers [17, 18], with examples drawn from the three areas—DNA, proteins, and biofuels—mentioned above.

2. Computational method

The SMC method and its implementation are described in detail elsewhere [15, 16, 17, 18], so here we only summarise key points. The SMC method is a variational procedure for the scattering amplitude which, by employing a many-particle trial wavefunction, allows electron exchange, target excitation, and polarisation to be accounted for naturally. Because the SMC variational expression is insensitive to the asymptotic behaviour of the wavefunction, a square-integrable trial function suffices; thus the underlying one-electron functions can be the Gaussian atomic orbitals of conventional bound-state quantum chemistry, facilitating integration with electronic structure codes and allowing application to arbitrary polyatomic molecules. The price one pays for these advantages is the occurrence of a Green's function term in the variational expression; evaluation of this term through numerical quadrature is the principal computational bottleneck. Fortunately, this step is amenable to efficient parallelisation [17, 18]. The parallel code uses a loosely synchronous model with distributed data and explicit message passing. The greater human effort required for initial implementation of such an explicitly parallel approach has been rewarded by the efficiency, robustness, and portability of the resulting code, which has performed well on a wide range of hardware, from tightly-integrated parallel supercomputers to networked clusters of personal computers.

3. DNA-related applications

Our studies of electron interactions related to DNA have mostly been directed at locating and characterising shape resonances that may play a role strand breaking. Pioneering measurements by Paul Burrow and co-workers identified three low-energy resonances in the electron-transmission spectra of each RNA and DNA nucleobase, which they assigned as the expected π^* resonances of aromatic-ring systems [19, 20]. Early calculations, however, placed the π^* resonances higher in energy [21, 22]. Thus an important question that could be addressed by carrying out high-level SMC calculations was simply whether the assignments of the observed resonances were correct. Scattering calculations on the nucleobases are rendered difficult not only by their size but also by their large dipole moments; however, after extensive trials with different one-electron basis sets and different many-electron variational spaces, a consistent picture emerged for each nucleobase. As an example, results for the pyrimidine base cytosine [23], obtained in collaboration with Sergio Sanchez, are shown in Fig. 1. The lower panel, showing the final results obtained with various Gaussian basis sets and slightly different representations of polarization effects, demonstrates that consistent predictions of the π^* resonance energies can be obtained despite the numerical challenges.

We have performed similar calculations for the purine nucleobases, adenine and guanine [24], as well as for the pyrimidine base uracil found in RNA [25]. Combined, these results support the resonance assignments of Burrow and co-workers; indeed, agreement between our results and their measurements is generally quite good for the energies of the two lowest resonances. For the third resonance, however, our calculated energies tend to be significantly (on the order of 2 eV) higher than the experimental positions. This is an unexpected result because polarisation effects should generally decrease in importance as the impact energy rises and the resonance broadens, both of which shorten the projectile–molecule interaction time.

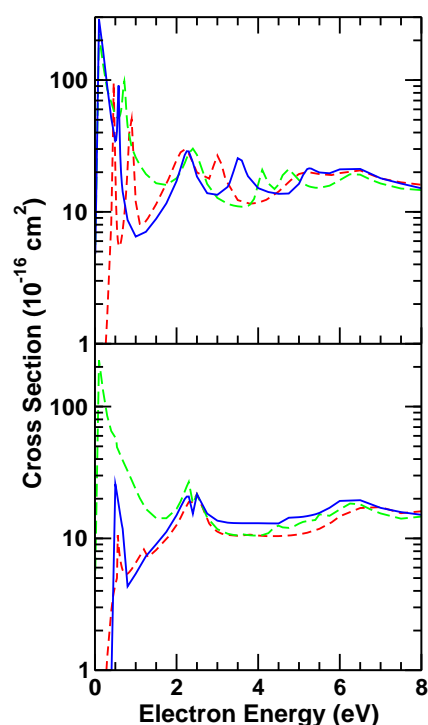


Figure 1. Calculated ${}^2A''$ component of the integral elastic cross section for electron scattering by the DNA nucleobase cytosine, showing the three π^* shape resonances as obtained in calculations using different one-electron basis sets. The bottom panel shows the final results, after controlling for numerical linear dependence. For details, see Ref. [23].

Subsequent investigation of the high-symmetry pyrimidine analogue pyrazine, $C_4N_2H_4$, identified the likely source of error. Our treatment of polarisation had focused on the perturbative response of the molecular charge density to the charge of the projectile electron, and had therefore emphasised singlet-coupled single excitations of the target molecule. However, pyrazine and other aromatic systems possess low-lying triplet excited states, raising the possibility of resonant channel mixing (continuum configuration interaction) between higher-lying shape resonances and core-excited resonances (shape or Feshbach) having the same symmetry. In fact, such channel mixing had already been posited by experimentalists [26] and observed in benzene [27]. Including appropriate triplet-coupled target excitations when building the SMC variational space for the third resonance of pyrazine shifted the peak energy much lower, bringing it into agreement with experiment comparable to that obtained for the two lower resonances. We thus plan to revisit the nucleobases to determine whether the same approach leads to similar improvements there.

For larger assemblies such as nucleosides (base plus sugar) and nucleotides (base, sugar, and phosphate), calculations that thoroughly address polarisation effects are difficult. However, static-exchange calculations, in which polarisation of the target molecule's charge density is neglected, are feasible for quite large molecules. Although the resonance positions resulting from such calculations will tend to be too high, one can compare results for the isolated nucleobases obtained with and without polarisation to derive resonance shifts due to polarisation. Those shifts may then be applied to the static-exchange resonance positions in the nucleosides and nucleotides to obtain estimates of the actual resonance positions. We have applied this approach to the four DNA nucleosides and to the nucleotide deoxyadenosine 5'-monophosphate [23, 24].

To explore the possibility of direct shape-resonant attachment to the DNA backbone, we have carried out SMC calculations on analogues of the sugar moiety, including tetrahydrofuran (THF) [28], 3-hydroxytetrahydrofuran (3HTHF) [29], and deoxyribose itself [28], as well as on phosphoric acid and its mono-, di-, and trimethyl esters [30]. Although elastic-scattering data on most of these systems are limited, our results for THF are in generally good agreement with other calculations [31, 32, 33] and measurements [34, 35, 36], and our 3HTHF results agree well

in shape with the measured differential elastic cross sections [29], though with some difference in magnitude. Interestingly, no shape resonances were found below about 5 eV in any of these backbone model systems, and the shape resonances that were found at higher energy were quite broad. Thus our calculations do not suggest an obvious mechanism for strand-breaking by direct dissociative attachment to the backbone. On the other hand, gas-phase measurements have observed low-energy dissociative attachment to deoxyribose [12] and to the dibutyl and triethyl esters of phosphoric acid [14]. It has been suggested [37] that gas-phase dissociation of models of the backbone sugar may depend on the presence of OH groups. Because OH groups are not found in DNA itself, THF, to which dissociative attachment is weak [38], would thus be the most appropriate model compound. Moreover, because O–H σ^* resonances are likely to be broad and high-lying at the equilibrium geometry, a mechanism involving them would be consistent with our SMC results showing no low-lying shape resonances, but it would also indicate that more caution is needed in interpreting such results, and indeed that calculations at multiple nuclear geometries may be necessary to obtain an accurate picture of resonant dissociation dynamics.

It should be mentioned however, that dissociative attachment was also observed at very low impact energies in 1,2,3,5-tetraacetylfuranose [13], a model chosen precisely for its lack of OH groups. Likewise, although our results are consistent with other calculations [33, 39] in finding no low-energy shape resonances in models of the phosphate moiety, weak resonances were observed at 2.1 and 4.6 eV in electron-transmission measurements on trimethylphosphate [40]. Thus many open questions remain about the importance of direct attachment to the backbone.

4. Protein-related applications

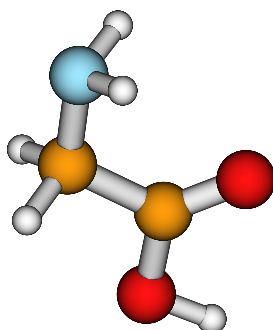


Figure 2. Structure of the simplest amino acid, glycine. Brown, red and blue spheres are carbon, oxygen, and nitrogen atoms, respectively, while the smaller white spheres are hydrogens.

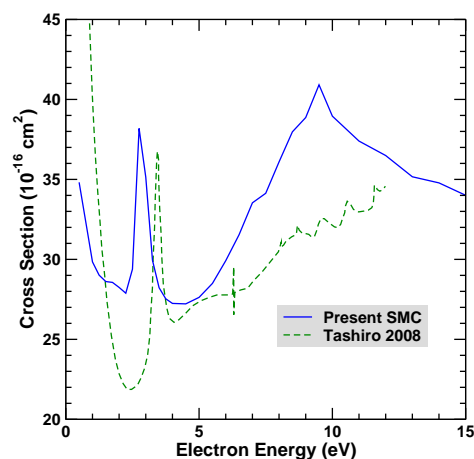


Figure 3. Integral cross sections for elastic scattering of low-energy electrons by the amino acid glycine. The solid curve represents preliminary SMC results for a conformer belonging to C_1 symmetry; the dashed curve represents the “CASSCF with Rydberg orbitals” results from the R -matrix calculation of Tashiro, Ref. [41].

Our protein-related collision studies are at an early stage. To date we have carried out preliminary calculations on one asymmetric (C_1) conformer of the simplest amino acid, glycine,

shown in Fig. 2 in a different, C_s -symmetric conformation. Our integral elastic cross section for the C_1 conformer is shown in Fig. 3 along with results from an R -matrix calculation by Tashiro [41] on the C_s conformer of Fig. 2. Both calculations show the $C=O$ π^* resonance as a prominent peak, although at somewhat different energies, each of which is above the reported experimental energy, 1.93 eV [42]. Some of the difference may be due to conformational effects, which in future work we will explore by repeating the fixed-nuclei scattering calculation for different conformers. However, the R -matrix calculations also demonstrated considerable sensitivity of the resonance energy to the representation of polarisation [41], and determining an appropriate polarisation space will therefore also be a focus in future work.

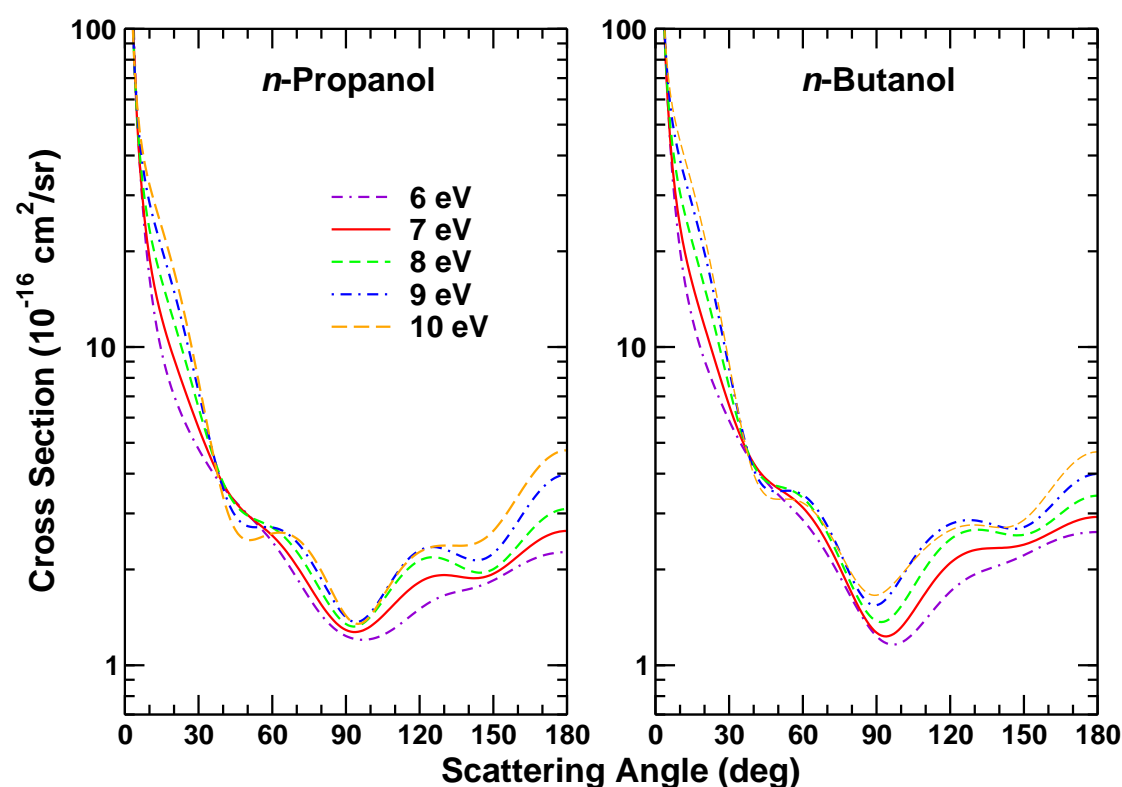


Figure 4. Differential cross sections for elastic scattering of electrons by n -propanol and n -butanol in the 6–10 eV energy range, from Ref. [44].

5. Alcohols

As mentioned in Sec. 1, cross sections for low-energy electron collisions with alcohols have applications in modeling the ignition and combustion of current and potential biofuels. However, studies of the alcohols are also of basic interest, allowing one to explore how electron-scattering patterns change (or persist) within a family of related compounds as the size and geometric structure of the molecules varies. In collaboration with experimental and computational scientists in Brazil and with the experimental group of Prof M A Khakoo at California State University, Fullerton, we examined elastic scattering by methanol, ethanol, n -propanol, and n -butanol [43, 44]. The differential cross sections revealed a striking similarity to a pattern previously seen [45, 46, 47, 48, 49, 50, 51, 52, 53] in the normal alkanes: over the energy range

where the integral elastic cross section rises to a broad peak (roughly 6 to 10 eV), the two-, three-, and four-carbon species show an *f*-wave scattering pattern, as shown for *n*-propanol and *n*-butanol in Fig. 4, while methane and methanol show *d*-wave patterns. Subsequent work on the isomers of butanol, carried out with Prof M H F Bettge (Federal University of Paraná), showed that the *f*-wave pattern is associated with straight chains, while branched isomers tend to the *d*-wave pattern seen in methanol and methane. Similar behaviour is again found in the corresponding alkane, with the branched isomer, isobutane, showing *d*-wave scattering [53].

To explore this trend further, we have recently, in collaboration with Profs Bettge and Khakoo, completed a joint computational and experimental study of isopropanol, CH₃–CH(OH)–CH₃. The results [56] appear to show a *d*-wave pattern, supporting the conclusion that the arrangement of the heavy atoms as a whole, rather than that of the carbon chain alone, determines whether a molecule behaves as “straight-chain” (*f*-wave) or “branched” (*d*-wave).

6. Conclusion

The examples above illustrate some of the progress that has been made in using *ab initio* computations to understand the electron collision dynamics of biomolecules. At the same time, they also suggest the need for much more extensive and detailed calculations to bring computations into closer contact with observations. In particular, a truly satisfactory understanding of dissociative attachment processes requires calculations that couple the electron-scattering dynamics to the nuclear dynamics. While such calculations are much more demanding than single-point fixed-nuclei calculations, they are beginning to be feasible for smaller molecules (e.g. [54, 55]), and may also be possible for larger molecules as long as only a few modes of nuclear motion are important. Addressing such coupled electron and nuclear dynamics will be a major emphasis in future applications of the SMC method to biomolecules.

Acknowledgments

This work was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, US Department of Energy under Grant No. DE-FG02-97ER14814, and in part by the US National Science Foundation under Grants No. 0653396 and 0968873. Calculations employed the Supercomputing and Visualization Facility at the Jet Propulsion Laboratory. We warmly acknowledge the contributions of theoretical and experimental collaborators to various aspects of the work reported here. In particular, work on the alcohols has been carried out within a Brazil-US joint project including Profs M H F Bettge, M A Khakoo, M A P Lima, M C A Lopes, and M T do N Varella, along with their respective research groups, while portions of the DNA-related work were carried out jointly with Profs M J Brunger, S J Buckman, and S d’A Sanchez, and their associates.

References

- [1] Boudaïffa B, Cloutier P, Hunting D, Huels M A and Sanche L 2000 *Science* **287** 1658
- [2] Boudaïffa B, Cloutier P, Hunting D, Huels M A and Sanche L 2002 *Radiat. Res.* **157** 227
- [3] Huels M A, Boudaïffa B, Cloutier P, Hunting D and Sanche L 2003 *J. Am. Chem. Soc.* **125** 4467
- [4] Sanche L 2005 *Eur. Phys. J. D* **35** 367
- [5] Berdys J, Anusiewicz I, Skurski P and Simons J 2004 *J. Phys. Chem. A* **108** 2999
- [6] Simons J 2006 *Acc. Chem. Res.* **39** 772
- [7] Barrios R, Skurski P and Simons J 2002 *J. Phys. Chem. B* **106** 7991
- [8] Berdys J, Skurski P and Simons J 2004 *J. Phys. Chem. B* **108** 5800
- [9] Anusiewicz I, Berdys J, Sobczyk M, Skurski P and Simons J 2004 *J. Phys. Chem. A* **108** 11381
- [10] Martin F, Burrow P D, Cai Z, Cloutier P, Hunting D and Sanche L 2004 *Phys. Rev. Lett.* **93** 068101
- [11] Li X, Sevilla M D and Sanche L 2003 *J. Am. Chem. Soc.* **125** 13668
- [12] Ptasińska S, Denifl S, Scheier P, and Märk T D 2004 *J. Chem. Phys.* **120** 8505
- [13] Bald I, Kopyra J, Dabkowska I, Antonsson E and Illenberger E 2007 *J. Chem. Phys.* **126** 074308
- [14] König C, Kopyra J, Bald I and Illenberger E 2006 *Phys. Rev. Lett.* **97** 018105

- [15] Takatsuka K and McKoy V 1981 *Phys. Rev. A* **24** 2473
- [16] Takatsuka K and McKoy V 1984 *Phys. Rev. A* **30** 1734
- [17] Winstead C and McKoy V 1996 *Adv. At., Mol., Opt. Phys.* **36** 183
- [18] Winstead C and McKoy V 2000 *Comput. Phys. Commun.* **128** 386
- [19] Aflatooni K, Gallup G A and Burrow P D 1998 *J. Phys. Chem. A* **102** 6205
- [20] Scheer A M, Aflatooni K, Gallup G A and Burrow P D 2004 *Phys. Rev. Lett.* **92** 068102
- [21] Gianturco F A and Lucchese R R 2004 *J. Chem. Phys.* **120** 7446
- [22] Tonzani S and Greene C H 2006 *J. Chem. Phys.* **124** 054312
- [23] Winstead C, McKoy V and Sanchez S d'A 2007 *J. Chem. Phys.* **127** 085105
- [24] Winstead C and McKoy V 2006 *J. Chem. Phys.* **125** 244302
- [25] Winstead C and McKoy V 2006 *J. Chem. Phys.* **125** 174304
- [26] Nenner I and Schulz G J 1975 *J. Chem. Phys.* **62** 1747
- [27] Allan M A 1982 *Helvet. Chim. Acta* **65** 2008
- [28] Winstead C and McKoy V 2006 *J. Chem. Phys.* **125** 074302
- [29] Vizcaino V, Roberts J, Sullivan J P, Brunger M J, Buckman S J, Winstead C and McKoy V 2008 *New J. Phys.* **10** 053002
- [30] Winstead C and McKoy V 2008 *Int. J. Mass Spectrom.* **277** 279
- [31] Trevisan C N, Orel A E and Rescigno T N 2006 *J. Phys. B* **39** L255
- [32] Bouchiha D, Gorfinkiel J D, Caron L G and Sanche L 2006 *J. Phys. B* **39** 975
- [33] Tonzani S and Greene C H 2006 *J. Chem. Phys.* **125** 094504
- [34] Colyer C J, Vizcaino V, Sullivan J P, Brunger M J, and Buckman S J 2007 *New J. Phys.* **9** 41
- [35] Allan M 2007 *J. Phys. B* **40** 3531
- [36] Dampc M, Milosavljević A, Linert I, Marinković B P and Zubek M 2007 *Phys. Rev. A* **75** 042710
- [37] Aflatooni K, Scheer A M and Burrow P D 2006 *J. Chem. Phys.* **125** 054301
- [38] Sulzer P *et al* 2006 *J. Chem. Phys.* **125** 044304
- [39] Bryjko L, van Mourik T, Dora A, and Tennyson J 2010 *J. Phys. B* **43** 235203
- [40] Burrow P D, Gallup G A, and Modelli A 2008 *J. Phys. Chem. A* **112** 4106
- [41] Tashiro M 2008 *J. Chem. Phys.* **129** 164308
- [42] Aflatooni K, Hitt B, Gallup G A and Burrow P D 2001 *J. Chem. Phys.* **115** 6489
- [43] Khakoo M A *et al* 2008 *Phys. Rev. A* **77** 042705
- [44] Khakoo M A *et al* 2008 *Phys. Rev. A* **78** 062714
- [45] Tanaka H, Okada T, Boesten L, Suzuki T, Yamamoto T and Kubo M 1982 *J. Phys. B* **15** 3305
- [46] Matsunaga D, Kubo M and Tanaka H 1981 *Proc. of the 12th International Conference on the Physics of Electronic and Atomic Collisions*, ed S Datz (North-Holland, Amsterdam) p 358
- [47] Curry P J, Newell W R and Smith A C H 1985 *J. Phys. B* **18** 2303
- [48] Tanaka H, Boesten L, Matsunaga D and Kudo T 1988 *J. Phys. B* **21** 1255
- [49] Sun W, McCurdy C W and Lengsfeld III, B H 1992 *J. Chem. Phys.* **97** 5480
- [50] Boesten L, Dillon M A, Tanaka H, Kimura M and Sato H 1994 *J. Phys. B* **27** 1845
- [51] Bettega M H F, da Costa R F and Lima M A P 2008 *Phys. Rev. A* **77** 052706
- [52] Lopes A R, Bettega M H F, Lima M A P and Ferreira L G 2004 *J. Phys. B* **37** 997
- [53] Bettega M H F, Lima M A P and Ferreira L G 2007 *J. Phys. B* **40** 3015
- [54] Rescigno T N, Trevisan C S and Orel A E 2008 *Phys. Rev. Lett.* **96** 213201
- [55] Adaniya H, Rudek B, Osipov T, Haxton D J, Weber T, Rescigno T N, McCurdy C W and Belkacem A 2009 *Phys. Rev. Lett.* **103** 233201
- [56] Bettega M H F, Winstead C, McKoy V, Jo A, Gauf A, Tanner J, Hargreaves L R and Khakoo M A 2011 *Phys. Rev. A* **84** 042702